APPLICATION OF CONCENTRATION OF ORGANOHALOGEN COMPOUNDS IN FLUE GAS FOR THE MANAGEMENT OF DIOXINS

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Introduction

There has been increasing demand for the monitoring of dioxins or dioxin surrogate compounds for the daily management of flue gas exhaust in municipal solid waste incinerators (MSWI). Various surrogates and measurement methodologies have been developed and shown (1-4). However, limitations in sampling procedure and analytical technique prohibit the selection of the most appropriate index. One idea is to use a rapid measurement method which is easy, quick, and cost-effective to analyze target chemicals. In this study, organohalogen compounds (OXs) determined by a non-specific method[1] were used as a useful alternative index of dioxins. This flue gas component was applied to real flue gas samples in MSWIs for the management of dioxins levels and its usefulness was discussed.

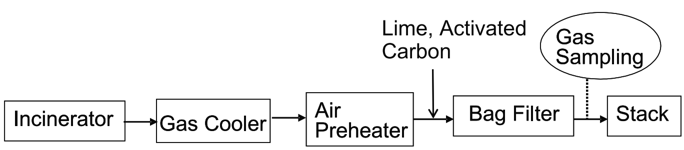

Figure 1. Incineration plant flow and gas sampling point of a semi-continuous incineration facility

Materials and Method

Flue gas Sampling

Flue gas sampling for determining organohalogen compounds by a non-specific method was performed according to the method formerly reported (1). The sampling was based on the adsorption of gaseous compounds by three activated carbon columns connected in series. Constituents that were absorbed or physically trapped by a drain were analyzed separately. Figure 1 shows the flow of the stoker type semi-continuous (16 hours operation per day) MSWI where many gas samplings were performed at the outlet of the bag filter. Lime and activated carbon mixtures were inserted into the duct before the inlet of the bag filter to remove dioxins and acidic gases such as HCl. Further measurements were also conducted in two stoker type continuous MSWIs, which were newly developed facilities and have boiler equipment instead of a gas cooler.

Experiments

Flue gas sampling was conducted under various experimental conditions in consideration of the

Table 1. Outline of experimental run conditions

Temperature (ºC)	Activated carbon dose (mg/m^3_N)	Combustion stability
160 - 200	50, 200	Normal
180	50 - 200	Normal
180	100 - 200	Unstable

influence of temperature at the bag filter inlet, activated carbon dose, stability of combustion and so on. Table 1 shows the outline of the experimental setups designed for the semi-continuous plant.

Analysis

Flue gas measurements were done for both dioxins and OXs on the samples taken simultaneously. Dioxins (PCDDs/DFs and Co-PCBs) were analyzed using HRGC-HRMS. OXs were analyzed using a TOX 100-Σ analyzer (Dia Instruments Co., Ltd., Japan) by burning activated carbon adsorbents whose inorganic halogen constituents had been rinsed before. Many kinds of halogenated organic compounds were transformed to halogenated hydrogen and the generated amount was determined by electrochemical titration, which leads to OXs expressed as chlorine amount in unit dry flue gas (μg-Cl/m^3_N).

Results and Discussion

Concentration of dioxins and organohalogen compounds

Table 2. Part of dioxins and OXs measurement data in flue gases

Temperature (ºC)	Activated carbon dose (mg/m^3_N)		Dioxins		OXs
		(ng/m^3_N@ 12 % O_2)	(ng-TEQ /m^3_N) [a]	(ng-TEQ /m^3_N) [b]	(**μ**g-Cl/m^3_N@ 12 % O_2)
165	45	6.6	0.0062	0.0058	100
180	54	14	0.036	0.13	130
198	57	53	0.41	0.42	100
164	61	5.7	0.0035	0.069	90
183	71	27	0.25	0.27	80
196	82	41	0.27	0.34	170
179	80	29	0.27	0.28	150
180	120	17	0.074	0.16	130
181	148	13	0.067	0.13	100
181	200	15	0.058	0.14	100

a: Numbers below the detection limit were calculated to be zero.
b: Numbers below the detection limit were calculated to be one-half of the limit.

Sixteen data of dioxins and organohalogen compounds concentrations were obtained for the semi-continuous plant and twelve data were obtained from two continuous plants. Table 2 shows the part of the data obtained in a semi-continuous plant. Dioxins concentration was approximately in the order of

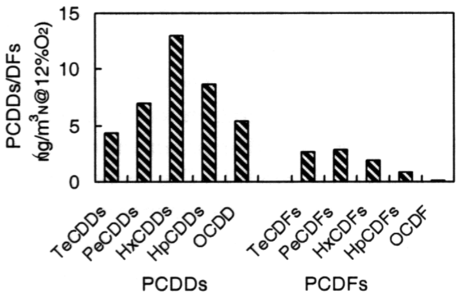

Fig. 2 PCDDs/DFs distribution profile

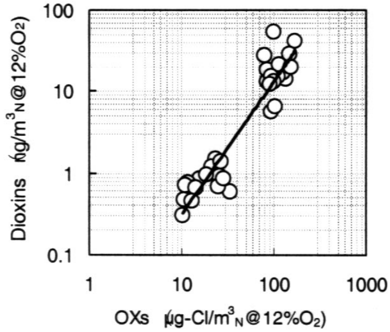

Fig. 3 Relationship between organohalogen compounds and dioxins in this experiment

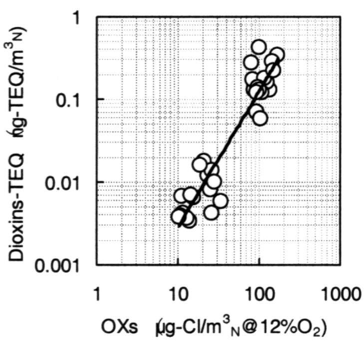

Fig.4 Relationship between organohalogen compounds and dioxins toxic equivalent in this experiment

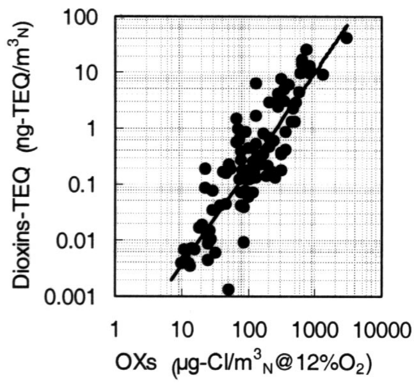

Fig. 5 Relationship between organohalogen compounds and dioxins toxic equivalent in this experiment

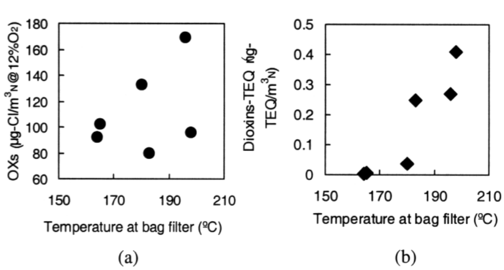

Fig. 6 Responses of OXs (a) and dioxins (b) concentration to the temperature at the inlet of bag filter

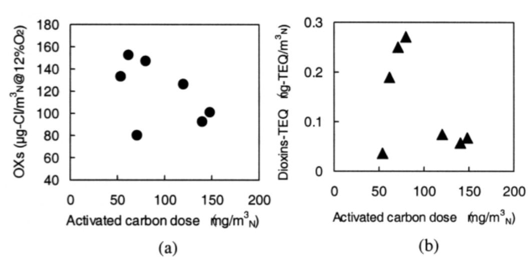

Fig. 7 Responses of OXs (a) and dioxins (b) concentration to the activated carbon dose

0.01 – 0.1 ng-TEQ/m^3_N. As there were some data below the detection limit, another calculation of toxic equivalent was performed. OXs concentrations ranged from 80 –to 170 µg-Cl/m^3_N@12-% O_2 for the semi-continuous plant, whereas the data in the continuous plants ranged from 10 -to 35 µg-Cl/m^3_N@12 % O_2. Considering that the OXs flue gas index may include volatile and semi-volatile organohalogen compounds[1], the values of OXs in Table 2 would demonstrate the existence ofs considerable amounts of organohalogen compounds which are 10^3 - 10^4 times the chlorine in dioxins molecules.

Qualitative profile of flue gas

Figure 2 shows a typical PCDDs/DFs homologue profile of the flue gas in the semi-continuous operation furnace. We could see almost the same profile for 16 flue gas samples for the semi-continuous furnace as shown in this figure, which consisted of major PCDDs and relatively minor PCDFs. This fact suggested that there were no big fluctuations in the composition of flue gas.

Relationship between Organohalogen Ccompounds and Dioxins

The correlation between organohalogen compounds concentration and dioxins would have great practical utility for a rapid decision-making of dioxins management. Figures 3 and 4 show the relationships we have obtained in this study. The plots in the relatively high concentration area were from the semi-continuous plant and the plots in the low concentration area were from thefull continuous plant. Recently, the actual concentration of dioxins is tending to decrease in newly constructed MSWIs. Therefore, a method for quickly and easily estimating low-level dioxins is needed. Figure 4 demonstrates that OXs measurement meets this need. Despite some scatter, the relationship shown in Fig. 5, which incorporates former data measured in a number of facilities, suggests that OXs measurement is useful for the daily management of dioxins in MSWIs by performing statistical processing of the accumulated data.

$$\text{Dioxins} = 0.0075\,(\text{OXs})^{1.63} \qquad (R^2 = 0.891) \tag{1}$$

$$\text{Dioxins-TEQ} = 1.7\text{E-05}\,(\text{OXs})^{1.78} \qquad (R^2 = 0.893) \tag{2}$$

Response of Organohalogen Compounds to Operation Parameters

Figures 6 (a) and (b) show the responses of OXs and dioxins concentration to the temperature at the inlet of the bag filter as an important operational parameters of MSWI. The concentration indices roughly increased with the increase of temperature, which suggested that OXs measurement could be used for estimating variations in dioxins concentration. Figures 7 (a) and (b) also shows the results for activated carbon dose, and a similar relationship is seen. One problem is that the variation range was different between two indices; hence, we must carefully consider how to use this parameter. Nevertheless, the index is useful for considering the daily operations of MSWIs.

Acknowledgements

The authors wish to extend sincere appreciation to NKK Corporation and Mitsubishi Heavy Industries, Ltd. for their provision of dioxins data in full continuous plants, and to Sanki Engineering Co., Ltd.. for their assistance in sampling flue gases in a semi-continuous plant.

References

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